Theory of Oil Tannage

With Special Reference to Seal Oil

DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY
OF PURE SCIENCE, COLUMBIA UNIVERSITY, IN
THE CITY OF NEW YORK

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BY

Bishan Narain Mathur, A. M.

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To Dr. Allen Rogers to Whom the Author Owes
His First Interest in Tanning This
Work is Dedicated

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Theory of Oil Tannage

With Special Reference to Seal Oil

By Bishan Narain Mathur, A. M.

The conversion of skin into leather by the agency of fats and oils is undoubtedly one of the most primitive methods used by the savage races in different parts of the globe. The various fat-containing substances derived from animals, fish and birds are used for this purpose. The usual oil-tanned leather is that which is produced simply by penetrating the oil into the fibrous structure of the skin. A typical example of such a leather is the ordinary shammy or chamois leather. This is made from the reticular layer (collagen) of sheep skin, which is split from the grain layer so that the two may be tanned separately for different purposes.

General Outline of the Process for Oil-tanned (chamois) Leather.

The skins which are to be converted into chamois leather are first—"limed," whereby they swell and the roots of the hair are loosened. After the hair is removed by the aid of a blunt dress-

ing knife, the unhaired skins are "drenched," *i. e.,* placed in a "sour bath," made of bran and water, in which they are neutralized in consequence of an acid fermentation (due to Bacterium furfuris) setting in. The unhaired skins after drenching are pickled with a solution of salt and dilute sulphuric acid and then allowed to press or drain over horses. The salt of the pickle acts as a deterrent to the progress of putrefactive processes and at the same time prevents the adhesion of the fibres by their complete separation. The pickled skins are next depickled by washing in plain water which causes a swelling of the fibres thus rendering it possible to accomplish a satisfactory splitting into a grain and flesh portion, known in the trade as skivers and fleshers. These skivers and fleshers are again pickled and may now be kept for an indefinite period before tanning.

In order to produce the chamois leather, the pickled flesh splits known as fleshers in a wet condition, are given an application of seal oil (cod liver oil, whale oil, or shark oil) usually mixed with a certain proportion of tallow. They are then run in "stocking machines" which distribute the oil uniformly throughout the porous structure of the skin. The fleshers are then taken out and allowed to oxidize. On becoming dry they are again moistened with water, rubbed with seal oil, and allowed to run again in the stocking machines. This process is repeated until the requisite oil has been absorbed. In practice the oil is usually applied three times or more on damp skins. In order to render the combination of the oil with the fibre more rapid, an "oxidation" attended with elevation of heat is sometimes brought about by heaping the skins together in a warm room, and covering them carefully with a canvas so as to conserve the generated temperature. Overheating, however, must be prevented by occasionally turning over the pile so as to cool the skins. The "oxidation" of the oil is considered to be complete when the skins have acquired the yellow color of the chamois leather. During the process of heating large quantities of volatile and very pungent products are given off, especially acrolein (acrylic aldehyde, from the dehydration of the glycerin), which is exceedingly irritating to the eyes. Some manufacturers, instead of piling the skins together, dry them slowly at a temperature of about 120° F. Leather is not produced as long as there is a considerable excess of water pres-

ent. In fact it is generally believed among practical tanners that the real tannage takes place at the time when the water is being expelled from the skin and complete tannage does not occur until the skin is almost dried. After tanning, the splits are soaked for a few hours in warm water (110° F.) and then pressed to remove uncombined oil, which is sold for leather dressing under the name of degras. The oil still adhering to the skins is removed by washing with a lukewarm solution (0.5 to 1 per cent) of sodium carbonate. The tanned skins are then washed with water, dried in air and after going through the different processes of staking, buffing, bleaching, and trimming, are packed in bundles to meet the demand of the market.

Chief Characteristic of an Oil-Tanned Leather.

1.—Oil tanned leather is soft and can be compressed in the hand like a piece of cloth.

2.—It is flexible and can be very easily bent, stretched or twisted.

3.—It is highly resistant to the action of water at ordinary temperatures.

4.—It is very durable and is not affected by the changes in weather. Oil-tanned furs, even after the elapse of a great many years, do not show any sign of deterioration.

5.—The oil tannage seems to be of an irreversible nature. Chrome tannage[1] can be almost entirely "stripped" in the cold by solutions of salts of dibasic organic acids such as potassium sodium tartrate. Vegetable tannage[2] can be "stripped" by a dilute solution of sodium carbonate, and the stripping action proceeds at an increasing rate if the pH value of the solution rises above 8. A piece of freshly tanned alum leather[3] can be deprived of its aluminum salts by mere washing. Formaldehyde[4] can be quantitatively recovered from leather by hydrochloric acid as weak as decinormal. But all attempts made so far to convert a

[1] Procter and Wilson. *J. Soc. Chem. Ind.*, 35, 156-9 (1916).

[2] Wilson, "The Chemistry of Leather Manufacture," P. 265, 323. Chemical Catalog Company (1923).

[3] Wilson, "The Chemistry of Leather Manufacture," P. 311. Chemical Catalog Company (1923).

[4] Proctor. *J. Soc. Leather Trades' Chem.*, 4, 282 (1920).

piece of oil-tanned leather into its original state of raw hide have met with failure.

Uses of Oil-tanned Leathers.

A.—Oil-tanned sheep splits or fleshers are used for
- (a) washing purposes;
- (b) the manufacture of vests, gloves, etc.;
- (c) filtering water out of gasoline;
- (d) lining shoes, bags, and cases;

B.—Oil-tanned buck skins are used for
- (a) gloves and sport shoes;
- (b) coats, riding breeches, leggings, piano hammers, etc.;
- (c) army purposes;

C.—Oil-tanned fur skins of superior qualities are used for
- (a) ladies coats;
- (b) neck-pieces, muffs, hats, scarfs, etc.;
- (c) trimmings of coats and shoes.

Different Views and Theories Regarding the Formation of Leather

1.—*Theory of Leather Formation by Knapp.*

It is now sixty-eight years since Friedrich Knapp of Germany, in a remarkable thesis[5] on the "Nature and Essence of Tanning" gave the first intelligible account of the nature of the change. According to his views the raw hide consists of a mass of fibres swollen with water, existing partly in the jelly of which the fibres consist, and partly retained by capillarity between them. If allowed to dry, the loosely held capillary water evaporates, and the gelatinous fibres come into contact while still moist and swollen, and adhere in a solid mass. If, on the other hand, the fibres can be made to give up the jelly water while still separated, they no longer adhere, but remain as a fibrous felt with all the physical characteristics of leather. Knapp accomplished this by treating the pelt with alcoholic solutions of gradually increasing strength,

[5] Knapp, Friedrich "Natur und Wesen der Gerberei und des Leders" Abhandlungen der naturwissenschaftlichtech. Commission bei der K. Akademie der Wissenschaften zu München. (1858).

finishing with absolute alcohol or a mixture of this with ether. This solution, in which the fibres are insoluble, gradually took the place of the capillary water, and then removed that held in the jelly, so that on finally evaporating the alcohol, no adhesion took place. The material obtained in this way was white, porous, and flexible and had all the outer characteristics of a white leather, but on soaking in water slowly turned to the raw hide condition. Knapp further found that a little stearic acid dissolved in the alcohol remained as a coating on the fibres and prevented or delayed their re-absorption of water. He carefully observed that the dehydration of the fibres, without adhesion, is necessary for the formation of leather. On these facts he based the theory that the essential of tanning is the coating of the fibres with some constituents of the tanning solution which will make them non-adherent, and he concluded that tanning was a mechanical rather than a chemical process.

2.—*Physical Theory of Oil Tannage by Kopecky.*

In the year 1907 Kopecky[6] proposed a physical theory of oil tannage according to which he considers oil-tanned leather to consist of ordinary fibrous hide substance having a coating of a fine film of oil completely covering the fibres, the oil film ensuring stability and resistance and giving the characteristics of leather to the hide. The writer considers the change in chemical nature (which is known to occur) of the oil used as of secondary importance. He claims that fat and oil tannage is a protective process preventing hydrolysis of the hide fibre, in which the omnipresence of the oil is more important than its state of oxidation.

3.—*Oil Tannage by R. B.*[7]

According to this theory, the fish oils and other fats used in chamois tannage (1) separate the bundles of fibres in the hide as do mineral tannins, (2) combine with the fibres as do vegetable tannins and at the same time (3) conserve the gelatinous fibres by changing themselves into aldehydes by oxidation. This state-

[6] F. K. Kopecky. *Collegium*, Nos. 268 and 269 (1907).

[7] R. B. *Gerber-Courier*, 55, No. 9, p. 1; abstract *J. Am. Leather Chem. Assoc.*, 9, 195 (1914).

ment is vouched for by Ganser and also by Proctor who bases the efficiency of oil tannage on aldehyde formation.

4.—*Theory of Leather Formation by Moeller.*[8]

In all tanning materials there are present two substances, a peptizer and peptizable substance, either of which is sometimes almost, but never entirely, pure. In vegetable tans, tannin is the peptizer and is found in both pyrogallol and pyrocatechol tans, while ellagic acid in the case of pyrogallol tan and phlobaphenes in the case of pyrocatechol tan, play the part of peptizable substances. It is to be noticed that ellagic acid and phlobaphenes are not obtained by splitting off from the tanning or catechol, but arise in the plant itself by condensation from the tannin, with the splitting off of pentoses and hexoses. In other words ellagic acid is a compound of pure acid with the peptizer, while catechol combines with the peptizer to form phlobaphenes. In tanning solutions, the peptized substance exists as an emulsion whose minute droplets consist of a core of peptizable substance, and a hull of compound of this with the peptizer. During the process of tanning, the peptizer forms solid solution with the hide fibre and is withdrawn from this hull by dialysis through the surface of the fibre, which forms a semi-permeable membrane. The freed peptized substance from the hull is then hydrolyzed during dialysis and deposits upon the surface of the fibre, where it unites, by condensation, along with the particles of the core and ultimately becomes crystalline; which marks the completion of the tanning.

So far we have considered an ideal case in which the peptizable material is supposed to be in a state of complete solution, but in general, especially in mineral tanning, there is either an excess of peptizer, when the peptizable substance is in true solution; or of the latter, when it is in the form of an emulsion. In the first case, the dissolved compounds of peptizable material would be hydrolyzed during dialysis, then an intermediate peptization on the surface of the fibre would occur, and, after the critical stage passes, condensation as explained above. But the tanning effect, as in the case of pure gall-nuts, would be small, because of the small amount of peptized substance. When there is a suspension, as in the second case, the amount of peptizer to be dissolved in

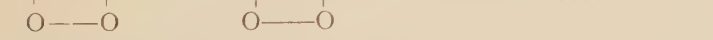
[8] W. Moeller. *Collegium*, 548, 441-57 (1915) 549; 1-16; 43-50; 125 7; (1916).

the fibre is relatively small, and a relatively large amount of peptizable substance, deposited and crystallized on the outside, would constitute the tanning. Moeller[9] considers oil tannage also in the light of his peptisation theory. He is of opinion, that fish oil contains substances very similar to lactones or acid anhydrides and that these substances readily combine with ammonia to form amino-acids. The ammonia required could be produced during tanning by a slight decomposition either of the skin or of the fish oil. By analysis an unhaired skin was found to contain 0.9 per cent nitrogen which was set free as ammonia by treatment of the skin with potassium hydroxide, while a fish oil contained 0.09 per cent of such nitrogen. The amino acids thus formed act as peptizers during the process of tanning. In 1922 Moeller[10] revised his views on the theory of tanning bringing them into harmony with the colloid chemical theory of P. Von Weimarn. He now considers that the mechanism of tanning consists in the destruction of the sol condition of the peptized solution by the substance of the hide. The hide substance removes the sol by absorbing the peptizing agent and the separated coagulated oil surrounds the micella of hide to form microcrystals. He summarises his conception of tanning and leather as; "Tanning materials are systems, of themselves insoluble, which form colloidal solutions by peptization." "Leather is animal hide whose elementary particles, in the form of crystaline micells, are protected from hydrolytic influences by being surrounded with tanning material."

5.—*Theory of Oil Tannage by Fahrion.*

According to Fahrion[11] the unsaturated free fatty acids containing at least two double bonds, are the active tanning agents of the fish oils in chamoising. These unsaturated acids perform the following functions during the process of tanning.

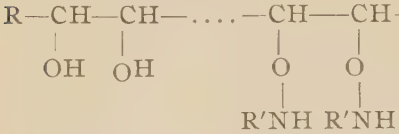
1.—Upon oxidation by the air these double bonded, free, fatty acids assume a di-peroxide structure represented by the formula.



.....(a)

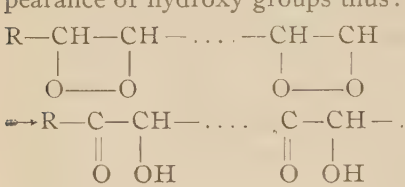
[9] W. Moeller. *Collegium*, 597; 12-17 (1920).
[10] W. Moeller. *Zeitsch. Led. Gerb. Chem.*, 1, 360 (1922).
[11] W. Fahrion. *Z. Angew. Chem.*, 665 (1903); 2083 (1911).

2.—A portion of the di-peroxide acids of formula (a) enters into combination with the protein matter of the hide substance. If we adopt the reduced formula $R'.N.H_2$ for the protein molecule, the reactions which come into play, yield, according to Fahrion, the complex.



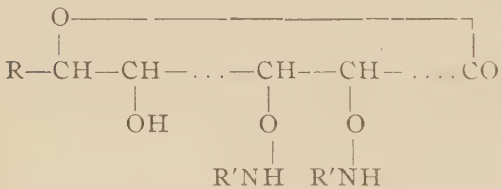
.....(b)

3.—The remaining portion of the di-peroxide acids of the formula (a) undergoes molecular rearrangement, causing the appearance of hydroxy groups thus:



.....(c)

4.—Finally in the complex of the formula (b) a lactonization is produced between the carboxyl group and the more distant hydroxy-group.



.....(d)

5.—The hydroxy acids of formula (c) also form lactones with the carboxyl groups. These lactones or "disguised fatty acids" are retained mechanically by the fibres, probably because they are insensitive to the alkaline washing which completes the manufacture of chamois leather.

6.—The aldehydes formed during the process of tanning probably also exert a tanning action on the skins.

6.—*Theory of Oil Tannage by Meunier.*

Meunier[12] observed that if a skin, previously dehydrated with alcohol, be tanned as for ordinary chamois, with an alcoholic solu-

[12] L. Meunier. *Chimie and Industrie,* 1; 71-80; 272-276 (1918).

tion of oleic acid, a soft leather is obtained, but after draining off the alcohol to remove the excess of oleic acid, the skin does not show any sign of being tanned when placed in water. Replacing the oleic acid by the fatty acids of colza oil which belong to the series $C_nH_{2n-4}O_2$ with two double bonds, which also includes a little linolenic acid $C_{18}H_{30}O_2$ with three double bonds, a yellow leather somewhat more resistant to the action of water is obtained. Substituting the fatty acids of linseed oil rich in linolenic acid, the leather obtained is still more resistant to water, but is inferior to that of leather prepared under the same conditions with the fatty acids of cod liver oil which belong to the series $C_nH_{2n-8}O_2$ and contain four double bonds in their molecules. Hence, according to Meunier;

(1) The tanning power of fish oil is due to the presence of free fatty acids possessing four double bonds of which at least two are capable of oxidation by the air, giving di-peroxides similar to those shown by the formula (a).

(2) Part of the di-peroxide acids react chemically with the protein matter, like quinone; one of the peroxide groups attacks the amino groups which are oxidized by loss of hydrogen; the hydrogen thus liberated transforms the oxygen of the second peroxide group into two hydroxy groups forming a complex similar to (b). Finally one of the hydroxy groups thus formed lactonizes the carboxyl of the fatty acids similar to (d).

(3) Another portion of di-peroxide acids by molecular rearrangements assumes the form of hydroxy acids similar to the formula (c). These hydroxy acids form lactones with the carboxyl groups. The disguised fatty acids or lactones thus formed are retained by the fiber, being resistant to the alkaline washing which completes the manufacture of chamois leather.

Tests and Observations

Two different samples of seal oil were obtained. The first oil, which was rendered from the fresh blubber of the Fur-Seal (Callorhinus Alascanus)[13] at the Pribilof Islands, Alaska, was of a pale yellow color. The second oil, which was extracted at a factory in St. Louis from blubber which had remained on the skins for several months, had assumed a very dark brown or

[13] Parker, Osgood and Preble. U. S. Bur. Fisheries. Doc. 820, p. 17 (1915).

almost black color. This difference in the colors of the oils as Proctor[14] indicates, was unexplainable. At first the factory rendered oil, designated hereafter as "Dark Oil," was rejected on the ground of its disagreeable appearance and thought to contain some undesirable impurities, but was later found to have higher tanning value than the oil prepared from the blubber of freshly killed seals. However, as the chemical composition of the "Dark Oil" is affected, as is explained later, by the climatic conditions and duration of time the blubber remains attached to the seal skins, it was thought advisable to use only the Island rendered oil for experimental purposes. Unless otherwise mentioned, the term "seal-oil" or "Pale Oil" will mean only the pure product of a light yellow color.

To determine the effect of aerating seal oil a sample which had been kept in a closed container for several months was used. This oil was of a pale yellow color, and outside of containing a very slight amount of moisture, was practically free from suspended matter. About 1000 cc. of this light colored oil was poured into a bottle and by means of an aspirator air was allowed to bubble through it at a constant speed. After the expiration of about 12 hours the oil acquired a brownish tint and changed its density from 0.907 to 0.910. From previous theories, it seemed at this time that the change in color and density of the seal oil might be due either to the formation of aldehydes or peroxy-acids or both.

In the study of the interaction of air-blown oil and hide-substance in the presence or absence of air, a pneumatic trough and a small bottle containing a piece of pickled skin in a moist condition were both filled with seal oil through which the air had been blown for about 12 hours. The glass bottle with capacity of about 260 cc. was then inverted into the pneumatic trough and nitrogen gas was introduced into the bottle by the upward displacement of the oil. When about 65 cc. of the oil remained in the bottle, its mouth was closed by means of a rubber stopper, while still under the oil. The air-tight bottle was then taken out of the trough and subjected to the rocking action of a shaker for about 14 hours. At the end of the operation a remarkable change

[14] Proctor. "Principles of Leather Manufacture," p. 447. D. Van Nostrand Co., New York, (1922).

was observed in the color of the oil. It had lost its brownish tint and, like the original seal oil, had again acquired its pale yellow color. The skin, however, showed no sign of tannage. The same experiment was repeated by substituting carbon-dioxide, and finally air, in place of nitrogen, but in all three cases the skin remained untanned while the brownish substance, produced during the process of aeration of the moist oil, seemed to be taken up by the hide substance. As large quantities of brownish substances are always found to be present in the "Dark Oil," it was thought advisable to compare its tanning power with that of the pure product ("Pale Oil") obtained from the fresh blubber.

In order to determine the relative tanning properties of the pale and dark oils rectangular pieces of pickled flesh splits were cut from the different parts of a sheep-skin and tanned separately with the two different oils. In each case the fleshers were moistened with water before receiving an application of the oil. They were dried at 120° F. and the same process was repeated until each piece had three applications of the oil. They were then washed with a dilute solution (0.5 per cent) of sodium carbonate, dried in the air at room temperature and subjected to the solvent actions of chloroform and ether. At the end of the operation samples of tanned splits, measuring one-half by five inches, which were quite free from uncombined oil were tested for their breaking ratios on a Perkins Tensile Tester. The results of the experiment are given in a tabular form and the breaking ratios clearly show that under similar conditions the "Dark Oil" produces a better piece of leather than the "Pale Oil."

TABLE SHOWING THE RELATIVE TANNING POWERS OF DARK AND PALE OILS.

Names of oils	Color of oil	% Of free fatty acids in the oils	No. of sheep fleshers	Average thickness of the fleshers (in. ins.)	Stretch %	Break (in. lbs.)	Breaking ratios Break / thickness
			A1	.026	28	22	846
Pale Oil	Pale Yellow	4.3	B1	.025	35	3	120
			C1	.026	28	17	654
			A2	.022	20	23	1045
Dark Oil	Darkish Brown	7	B2	.024	24	16	667
			C2	.023	22	22	956

NOTE:—Pieces of pickled sheep fleshers marked A1 and A2 were cut from the head end of the skin; B1 and B2 were cut from the tail end of the skin; while C1 and C2 were selected from both ends.

Should the superior tanning properties of the "Dark Oil" be even partly due to the higher percentage of free fatty-acids (see Table), and further, should free fatty acids be capable of forming leather, then such facts would disprove the theory that chamois leather is formed by the aldehydes resulting from the decomposition of the glycerine radical. In order to determine this point about two gallons of the "Pale Oil" was saponified in a steam jacketed kettle and the soap thus formed was salted out and separated from the excess of alkali. The soap of the seal oil was then decomposed with dilute hydrochloric acid and the free fatty acids were removed. The luke-warm mixture of these acids was then allowed to stand over night in a glass jar and on the next day about 16 per cent of the acids were found precipitated at the bottom of the vessel. These acids, consisting of saturated acids of high melting points, were discarded and the unsaturated acids were drawn from the top and used in the experiment.

A pack of pickled sheep fleshers containing half a dozen of flesh splits was moistened with water and the moist pieces were thoroughly soaked with the liquid acids of the seal oil. These fleshers were then subjected to the tumbling action of a closed drum for about three hours. On opening the drum no pungent odor was apparent, showing thereby that the irritating smell of acrolein, which at this stage of the process is always given off whenever straight seal oil is used for chamoising leather, was entirely wanting. Signs of partial tannage were visible on the surfaces of the fleshers. These partially tanned fleshers were then dried at 120° F. to hasten the action of chamoising. On becoming dry they were again moistened with water and a second coat of unsaturated acids was applied to their surfaces. The six fleshers were then hung in a dryer the temperature of which during the night time fell from 120° F. to 80° F. On the next morning the fleshers were found to be in a dry and tanned condition. All of them had acquired the characteristic yellow color of chamois leather. The uncombined portion of the fatty acids was then removed from the fleshers by treating them with a luke-warm solution (0.5 per cent) of sodium carbonate. In the end the fleshers were washed with plain water and dried in air. The fleshers thus tanned had all the characteristic qualities of leather, but for want of lubrication lacked softness and pliability. Whatever may be

the real nature of the tanning substances, the results of this experiment clearly show that acrolein has nothing to do with the chamoising of the leather and that the unsaturated fatty acids have a tanning value.

Practically all of the present theories of oil tannage are based on the assumption that the oil is oxidized during the tannage and that the products of oxidation react in some way with the hide fibre to form leather. This being the case, it is logical to assume that leather will be more easily and readily formed if the oxidation of the oil is accomplished before it is applied to the hide fibre. The tanning power of seal oil in an oxidized condition was therefore tested in the following manner. About 50 cc. of seal oil were heated in a beaker to about 120° C. to drive out the moisture. The oil was then poured into a watch crystal and allowed to oxidize in a dryer at about 180° F. After a week or so the oil was found to be in a fairly thick condition and unlike the moist oil was quite free from brownish substances, being quite light in color. A small rectangular piece of pickled sheep flesher was moistened with water and given an application of the oxidized oil. The piece was then dried at 120° F. and the same process was repeated a second and third time. The piece was then washed with a dilute solution (0.5 per cent) of sodium carbonate and dried in air. This air-dried piece did not show any appreciable sign of tannage. It was hard and stiff and cracked on twisting. The experimental results, therefore, show that seal oil, oxidizing in the presence of air but in the absence of moisture, is not capable of producing materials useful for tanning purposes.

In order to determine the role of water in the process of tanning, the unsaturated fatty acids obtained from seal oil were thoroughly rubbed on both sides of a moist pickled sheep flesher. The skin was then placed in a warm room. On becoming dry it acquired a yellowish tint. This partially tanned flesher was then spread on a drawing board and two concentric circles drawn on its surface at a place where the yellowish tint of the hide fibres was found to be of a uniform depth. The inner circle was moistened and the flesher again placed in the warm room. During the night the faint coloration of the inner circle was changed into the bright typical yellow color of a well tanned chamois skin. This portion of the flesher showed normal strength while the light

colored portion was weak. The contrast of the deep yellow color of the inner circle with that of the faint and unchanged yellowish coloration of the outer ring was convincing proof that water plays a very important part in oil tannage. It has, however, never been considered in discussion of the aldehyde or peroxide theories. To gain some light on the action of water during tanning the following test was made.

An air-dried pickled flesher was thoroughly soaked with unsaturated fatty acids from seal oil, and was dried in a warm room. During the first few days no appreciable amount of tannage was visible and it was only after several days that the characteristic yellow color of the chamois leather made its first appearance. The air-dried flesher which had but a limited amount of firmly held water within its fibres was no doubt tanned, but the hide substance had lost much of its original strength. The same experiment was repeated by substituting seal oil in place of unsaturated fatty acids, but the results in both cases, in so far as the weakening of the hide fibres is concerned, were the same. This shows that hide substance in order to be converted into a strong leather must have a certain amount of moisture present during the tanning process.

That the behavior of water during the process of oxidation might be observed, two rectangular pieces, 5″ x 9″ were cut from a piece of heavy canvas which had been thoroughly washed with boiling water. The piece marked A was dried in a current of hot air, while the other marked B was moistened with water. Both pieces were then separately soaked in 20 grams of unsaturated acids which had been previously obtained by the decomposition of seal oil. These rectangular pieces of cotton cloth were hung in a dryer and the unsaturated acids of seal oil allowed to oxidize in a current of air at about 120° F. During the process of oxidation the piece marked A was allowed to remain in its original dry condition, but the piece marked B was moistened several times with water. After 24 hours, when the pieces were taken out of the dryer, the following change was observed. The piece marked A was still oily to the touch and no change was noticeable in its appearance, but the piece marked B was quite dry and its fibres appeared as if painted with a dull orange-colored pigment. Both pieces were washed with a dilute solution (0.5

per cent) of sodium carbonate. The piece marked A was very quickly deprived of its oily coating and became perfectly clear, while the orange coating in sample B was only removed with difficulty by repeated washing. The unsaturated fatty-acids of seal oil, therefore, in the presence of air and water form compounds quite different from those produced in an atmosphere of dry air only. The same experiment was repeated with free fatty-acids obtained from linseed oil and cod-liver oil, but in all cases the products of oxidation formed in the presence of moisture differed widely from those formed under the influence of dry air alone.

To study the tanning effects of seal oil on hide fibres under different conditions of moisture, approximately fifty gallons of seal oil containing about 10 per cent of moisture were kept in a state of constant agitation for about 48 hours. A centrifugal pump was used for this purpose and during all the time the oil coming out of the pump in the form of a spray was made to pass over and over again through the pump. A further arrangement was made for the water to drip over the spray of oil at the rate of about one pint an hour. Samples of oil were taken at different intervals and their iodine values determined. Rectangular pieces of pickled fleshers were tanned separately with these various samples. In the first case, according to the usual custom three applications of water along with three applications of oils were given to the fleshers, but in the second case an extra application of water was given to the dry fleshers in the end, and also between the two successive applications of the oils. In other words, the fleshers in the second case got six applications of water and three of oil. The results of the experiment are given in a tabular form and a close examination of the breaking ratios throw some light on the chemical behavior of water.

In the experiments herein recorded the thing which stands out as differing from the ideas of leather tanning commonly held, is the chemical behavior of water. It was conceived that water might enter into combination to form hydroxyacids and if this is so it may explain some of the points now open to question. With a hope of getting definite and reliable information an attempt was therefore made to convert the liquid unsaturated acids of the seal oil into hydroxy-acids of a solid nature.

TABLE I.—Table Showing the Tanning Effects of Seal Oils Under Different Conditions of Moisture.

(Fleshers receiving 3 applications of water and 3 of oils).

No. of different oils	No. of different fleshers	Iodine values	Average thickness of the fleshers (in inches)	Stretch %	Break (in lbs.)	Breaking ratios Break / thickness
1	A1	134	.019	48	5	263
2	A2	112	.015	40	7	467
3	A3	130	.017	38	5	294
4	A4	120	.021	50	2	95
5	A5	119	.023	42	5	217
6	A6	114	.022	42	7	318
7	A7	110	.020	47	15	750
8	A8	109	.026	36	14	538
9	A9	91	.025	18	20	800
1	B1	134	.021	34	3	143
2	B2	112	.020	37	16	800
3	B3	130	.025	44	11	440
4	B4	120	.022	40	12	545
5	B5	119	.022	38	7	318
6	B6	114	.022	43	3	136
7	B7	110	.020	39	5	250
8	B8	109	.023	38	2	87
9	B9	91	.022	42	3	136
1	C1	134	.023	22	17	739
2	C2	112	.034	34	23	676
3	C3	130	.030	26	21	700
4	C4	120	.029	20	15	517
5	C5	112	.020	32	15	750
6	C6	114	.020	17	10	500
7	C7	110	.020	13	15	750
8	C8	109	.028	19	15	536
9	C9	91	.023	24	17	739

N. B.—Oil No. 1 is pale oil; Oil No. 2 is dark oil; while oils Nos. 3, 4, 5, 6, 7, 8, and 9 are the samples of pale oil taken at different intervals of time during 48 hours. Pieces of pickled sheep fleshers marked A1, A2, A3, etc., were cut from the head end of the skin; B1, B2, B3, etc., were cut from the tail end of the skin; while C1, C2, C3, etc., were selected from both ends.

TABLE II.

(Fleshers receiving 6 applications of water and 3 of oils).

No. of different oils	No. of different fleshers	Iodine values	Average thickness of the fleshers (in. inches)	Stretch %	Break (in lbs.)	Breaking ratios $\frac{\text{Break}}{\text{thickness}}$
1	A1	134	.030	54	17	567
2	A2	112	.026	48	15	577
3	A3	130	.027	52	15	556
4	A4	120	.030	48	18	600
5	A5	119	.031	58	20	645
6	A6	114	.034	45	26	765
7	A7	110	.035	62	32	914
8	A8	109	.029	66	16	551
9	A9	91	.030	66	25	833
1	B1	134	.025	55	18	720
2	B2	112	.035	62	35	1000
3	B3	130	.030	63	25	833
4	B4	120	.032	54	20	625
5	B5	119	.030	60	16	533
6	B6	114	.027	50	18	667
7	B7	110	.028	58	17	607
8	B8	109	.031	53	28	903
9	B9	91	.025	68	22	880
1	C1	134	.021	57	17	810
2	C2	112	.028	76	19	679
3	C3	130	.028	58	25	893
4	C4	120	.032	58	27	844
5	C5	119	.027	66	22	815
6	C6	114	.029	60	22	759
7	C7	110	.022	49	10	455*
8	C8	109	.024	44	15	625
9	C9	91	.020	45	15	750

N. B. In all cases the rectangular pieces of the tanned fleshers were reduced to the same size (½" x 5") before actually running the test.

* The flesher marked C7 seemed to have some natural defect and was consequently broken under the comparatively small force of 10 lbs.

We know that according to Hazura's Rule,[15] the unsaturated acids on being oxidized with potassium permanganate in a dilute alkaline solution, absorb as many hydroxyl groups as they possess free valencies; and that by so doing they yield saturated hydroxy-acids which always contain the same number of carbon atoms as

[15] Hazura. *Monatsh.*, 8, 260 (1887).

the original acids. Following out this law, 30 grams of unsaturated fatty-acids from seal oil were saponified with 30 cc. of an aqueous solution of potassium hydroxide having a specific gravity of 1.28. The soap thus formed was dissolved in 2 liters of water and treated with 2 liters of a 1.5 per cent solution of potassium permanganate. The oxidation was stopped after ten minutes with the help of a reducing agent. Sulphurous acid used for this purpose was added in sufficient quantity to make the solution acid and to dissolve the manganese oxide produced by the reduction of potassium permanganate. To avoid an excess of sulphurous acid which is liable to change the constitution of hydroxy-acids, the end point was considered to be reached when a few drops of the solution on a filter paper distinctly showed brownish precipitates without any coloration in the liquid. The mixture of solid hydroxy acids thus formed was filtered off, dried in air and thoroughly washed with absolute alcohol. The portion soluble in alcohol, consisting of unoxidized acids, was discarded, while the solid hydroxy acids purged from adhering impurities, was used for experimental purposes.

A small rectangular piece of pickled sheep flesher was moistened with water and a few grams of the solid hydroxy acids thoroughly rubbed on its surface. The piece was then dried at 120° F. and the same process repeated a second time. In the end the uncombined portion of the dark hydroxy acids was thoroughly removed by repeatedly washing with a luke-warm solution (0.5 per cent) of sodium carbonate. The piece was then air-dried. On close observation, the surface of the dried flesher was found to have lost the jelly-like structure which is an inherent property of an untanned skin. The surface fibres had assumed a brownish appearance and although the intensity of the color in this case was not of the same depth as is generally seen on the surface of a well-tanned chamois skin; yet the signs of chemical action were visible. The same experiment was repeated by substituting unsaturated acids obtained from linseed and olive oils in place of those obtained from seal oil, and in all three cases the surface fibres acquired a light brown color. The experimental results, therefore, at this stage of the investigation, suggest that the carboxyl (COOH) groups of the unsaturated fatty acids do not undergo any chemical change during the process of tanning

and that the hydroxyl (OH) groups produced during the process of oxidation do unite chemically with the hydrogen of the hide substance with the elimination of water. For the elucidation of these phenomena the next attempt was therefore made to tan a piece of skin under conditions most unsuitable for the formation of lactones.

About two gallons of seal oil were thoroughly saponified in a steam jacketed kettle with an excess of sodium hydroxide and the sodium salt thus formed salted out three times from its aqueous solution. The soap thus produced was then used for experimental purposes .

A small rectangular piece of a pickled sheep flesher was moistened with water and a few grams of the purified soap, previously dissolved in a small amount of water, was thoroughly rubbed on its surface. The piece was dried at 120° F. and the process repeated until three applications of the pasty soap solution had been given to the flesher. The dried flesher was treated with a lukewarm (110° F.) solution (0.5 per cent) of sodium carbonate and was finally washed with distilled water. It was then dried in air and the air dried flesher subjected to the solvent actions of chloroform, ethyl ether, ethyl alcohol, carbon bisulphide, carbon tetrachloride, and petroleum ether, respectively. At the end of these operations the fibres of the flesher were found to assume the characteristic yellow color of an oil tanned skin. Their tensile strength was largely increased, they were soft and flexible, and had acquired all the distinguishing properties of chamois leather. The same experiment was repeated by substituting soaps prepared from cod liver oil, and shark liver oil in place of that obtained from seal oil, and in all three cases the fleshers were found to be in a well tanned condition. Experiments were also conducted on unpickled pelts, and in each and every case the above mentioned soaps produced satisfactory leather. It is known that the presence of free unsaturated acids is essential to the formation of lactones; and that soaps, being compounds of a more stable nature, cannot decompose into the unsaturated fatty acids from which they are formed unless subjected to the chemical actions of strong acids. It is, therefore, evident that soaps of unsaturated oils, while chamoising fleshers under the conditions specified, cannot change into lactones. Therefore the prevailing idea that lactones

play any part in the tanning of leather, simply because of their resistance to alkaline washing and their retention by the fibres of the hide substance, is only a mere guess in the absence of any experimental proofs. Although lactones are not formed during the process of tanning, the formation of peroxides or aldehydes and their possible function in chamoising leather was still a problem which needed an adequate solution and a satisfactory explanation based on experimental proof.

Experiments were now conducted to ascertain the changes which soaps prepared from seal oil, cod liver oil, and shark liver oil, undergo under different conditions of moisture. A few grams of the moist soap prepared from seal oil was pressed several times within the folds of filter papers to remove nearly all the moisture. The fairly dry soap thus obtained was rubbed on the surface of a rectangular piece (marked A) of cotton cloth previously cut from one of the corners of an ordinary well-washed towel. From the opposite corner of the same white towel another rectangular piece (marked B), similar in size to that of A, was cut, but unlike the rectangular piece marked A, it was soaked in water and then an application of the moist soap prepared from seal oil given to its wet surface. Both pieces were then hung in a dryer whose temperature was kept at 120° F. During the process of drying the rectangular piece marked A was allowed to remain in its original dry condition, but the rectangular piece marked B was moistened several times with water. After 24 hours, when the pieces were taken from the dryer, the following change was observed. The soapy film, as well as the cotton fibres of the piece marked B had assumed a brownish appearance, but no brownish substance was noticeable on the piece marked A. Both pieces were then washed with distilled water. In a few seconds the soapy particles of a pale yellow color were removed from the surface of the piece marked A, leaving it in a clean condition. In the piece marked B the brownish particles of the changed soap were held tenaciously by the cotton fibres and it was with considerable difficulty by constant washing, that it was made to assume its original white color. The same experiment was repeated by substituting soaps prepared from cod liver oil and shark liver oil in place of that

obtained from seal oil.* In all three cases the results obtained were similar to those on samples A and B, mentioned above.

These experiments therefore give unmistakable evidence that sodium-salts, of the unsaturated fatty acids obtained from seal oil, cod liver oil, and shark liver oil, in the presence of air and moisture form compounds quite different from those formed in an atmosphere of dry air alone.

To ascertain the tanning power of the brownish compounds prepared from the sodium salts of the acids present in seal oil, cod liver oil, and shark liver oil, about 1,000 grams of the purified sodium salt (the soap) which was prepared from seal oil was moistened with water and exposed to air in the form of small chips. These chips on becoming dry were again moistened with water and the same process repeated over and over again until all the chips from within as well as from without were turned brown. This mixture of brownish compounds containing probably a small amount of soap in an unchanged condition was then used for experimental purposes.

A rectangular piece of a pickled sheep flesher was moistened with water and a few grams of the brownish compound previously dissolved in a small amount of water was thoroughly rubbed on its surface. The piece was dried at 120° F. and the process twice repeated. The dried piece was then treated with a lukewarm (110° F.) solution of sodium carbonate (0.5 per cent) and finally washed with distilled water. When dried in air its fibres were found to have the characteristic yellow color of an oil tanned skin. The flesher had become soft and flexible, with all the distinguishing properties of chamois leather. The same experiment was repeated by substituting the brownish soaps formed under the influence of moisture from the sodium salts prepared from cod liver oil and shark liver oil in place of that obtained from the sodium salt of seal oil, and in all three cases the air dried fleshers were found in a tanned condition. These results, therefore, show that the brownish compounds developed in air under the influence of moisture possess the power of tanning hide substance

In order to determine the tanning power of brownish soap prepared from seal oil in a chemically pure condition, the mixture of

* It is to be noticed that the soap prepared from the linseed oil which has comparatively a poor tanning value also turns brown in the presence of moisture.

brownish compounds prepared in the last experiment by the action of moisture on the soap from seal oil, was decomposed on the water bath by a dilute solution of hydrochloric acid. The product of decomposition, consisting chiefly of brownish precipitates was washed several times with distilled water in order to remove the excess of mineral acid. The insoluble solid acids were then dried on a porous tile and extracted with petroleum ether. The residue from the ethereal extract was of an oily nature and consisted probably of the unoxidized portion of the fatty acid. The brown colored precipitate, insoluble in petroleum ether was then used for experimental purposes.

Twenty grams of the brown precipitate was partially saponified with an aqueous solution containing two grams of sodium hydroxide. The soap thus formed was passed while hot through a filter paper. The filtrate was evaporated on a water bath to a pasty consistancy. A rectangular piece of pickled sheep flesher was moistened with water and a few grams of the pasty soap solution was thoroughly rubbed on its surface. The piece was dried at 120° F. and the process twice repeated. The dried piece was then treated with a lukewarm (110° F.) solution (0.5 per cent) of sodium carbonate, and finally washed with distilled water. It was then dried in air and subjected to the solvent actions of ether, chloroform, and alcohol, respectively. At the end of all these operations the fibres of the flesher were found to assume the characteristic yellow color of an oil tanned skin. They were soft and flexible and had acquired all the distinguishing properties of chamois leather. These experimental results, therefore, show that the sodium salts of the unsaturated fatty acids present in seal oil, without undergoing any change in the carboxyl (COONa) group develop in the presence of air and moisture into compounds essential for the chamoising of hide substance.

To determine the tanning powers of the solid acids prepared by the decomposition of brownish soap obtained from the seal oil, a few grams of the solid acids prepared in the above experiment were dissolved in alcohol and the brownish solution thus produced was used for experimental purposes. A rectangular piece of pickled sheep flesher was moistened with water and the alcoholic solution of the solid acids thoroughly rubbed on its surface. The flesher was dried in the air at room temperature and the same

process was repeated ten or twelve times. The air dried piece was then treated with a lukewarm (110° F.) solution (0.5 per cent) of sodium carbonate and finally washed with distilled water. It was again dried in air and the air dried piece was subjected to the solvent action of alcohol, ether, chloroform, and petroleum ether, respectively. At the end of all these operations the fibres of the fleshers were found to have the characteristic yellow color of an oil tanned skin. The results of all these different experiments therefore, clearly prove that the unsaturated acids of seal oil in the presence of air and moisture form solid acids of brownish color and that these solid acids as well as their sodium salts possess the power of chamoising hide fibres. It was also found that potassium and even the lead salts of the unsaturated acids in seal oil, in the presence of moisture and air tan hide substance. This makes it further quite conclusive that the carboxyl (COOH) groups of the unsaturated acids do not enter into any chemical reaction during the process of tanning, but that the hydroxyl (OH) of the moisture seems to be responsible, in one way or the other, for bringing about the phenomenon of the change from the harsh fibres of hide substance to the soft ones of pliable leather.

In order to discover the presence of such a hydroxyl group the next attempt was therefore made to analyse the colored compounds which form in the presence of moisture. About 20 grams of the solid acids, isolated from the brownish soap of the seal oil, were partially saponified with an aqueous solution containing two grams of sodium hydroxide. The soap thus formed was filtered while hot. The brownish filtrate evaporated to dryness on a water bath, and the dried soap thus obtained was used for experimental purposes.

About five grams of the dried soap was thoroughly agitated in a large beaker with toluene and solid pieces of phosphorus penta-chloride gradually added to the mixture. As a result the brownish soap was changed into a gummy material of a dark color, while the toluene remained unchanged. It is a well known fact that phosphorus penta-chloride replaces the hydroxyl (OH) of both the alcoholic and the acidic function with Cl. By the action of phosphorus penta-chloride on hydroxy-acids, or their salts,[16]

[16] Moureau, "Fundamental Principles of Organic Chemistry translated from the sixth French Edition by Braunholtz," p. 232. G. Bell and Sons, Ltd., (1921).

therefore, the alcoholic function is converted into that of hydrochloric ester (chloro derivative) and at the same time, the acidic function into that of an acid chloride; *e. g.*:

$$\underset{\text{Sodium lactate}}{CH_3\text{–}CHOH\text{–}COONa} + 2PCl_5 \longrightarrow \underset{\text{a-chloropropionyl chloride}}{CH_3\text{–}CHCl\text{–}COCl} + NaCl + HCl + \underset{\text{Phosphorus oxychloride}}{2POCl_3}$$

It should be further noticed that the acid chloride function[17] is very readily decomposed by water even in the cold state, whereas the hydrochloric ester function is much more resistant; *e. g.*:

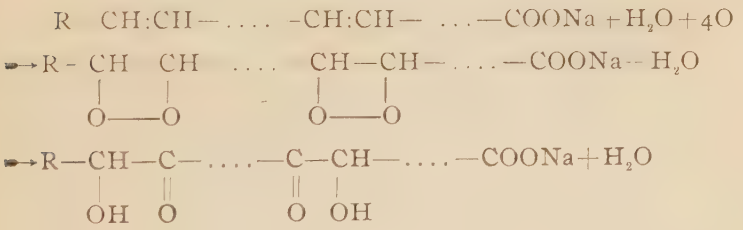
$$\underset{\text{a-chloropropionyl chloride}}{CH_3\text{–}CHCl\text{–}COCl} + H_2O \longrightarrow \underset{\text{a-chloropropionic acid}}{CH_3\text{–}CHCl\text{–}COOH} + HCl$$

Taking these points into consideration, a quantity of distilled water was added to the beaker and by so doing the gummy material was changed into an oily liquid which was found to be fairly soluble in toluene. The contents of the beaker were then transferred to a separatory funnel and the layer of the toluene was washed several times with distilled water. The wash water containing hydrochloric acid, phosphoric acid, and sodium chloride in solution, was drawn every time from the bottom of the separatory funnel and was discarded. The washing was continued until the wash water was found free from Cl ions. When all the soluble impurities were removed, the toluene containing the newly formed organic acid in solution was transferred to a one liter flask in which about 100 cc. of a 10 per cent solution of silver nitrate and approximately 200 cc. of concentrated nitric acid had already been poured. The flask was heated on the flame of a Bunsen burner and the volume of its contents was reduced to about 100 cc. Toluene and water were removed by evaporation while the organic acid was completely decomposed by the oxydizing action of nitric acid. It should be noticed here that chlorine, if liberated during the decomposition of organic acid, forms silver chloride, and in order to detect its presence the contents of the flask on becoming

[17] Moureu, "Fundamental Principles of Organic Chemistry translated from the sixth French Edition of Braunholtz," p. 243. G. Bell and Sons, Ltd., (1921).

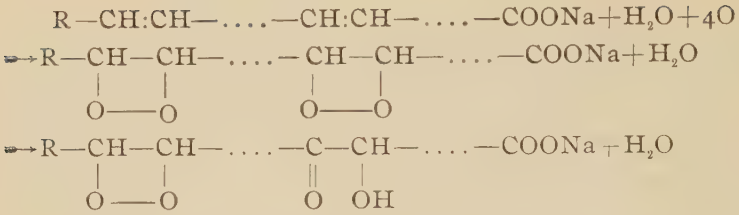
cold were diluted with 100 cc. of distilled water and then made alkaline by the addition of Ammonium hydroxide. About 50 cc. of the solution were poured into a beaker. This ammoniacal solution at first looked clear but soon became turbid on the addition of a few drops of nitric acid. The white precipitates causing turbidity were found to be soluble in ammonium hydroxide but insoluble in nitric acid. This distinguishing property of the precipitates clearly proved the formation of silver chloride. The phosphorus penta-chloride under these conditions must have replaced the OH of the alcoholic function by Cl. It is therefore evident that the unsaturated acids or their sodium salts obtained from seal oil in the presence of air and moisture changed themselves into brownish compounds which contain at least one OH group of an alcoholic function in their chemical compositions. It has already been shown that these solid hydroxy acids and their salts possess the power of chamoising leather, but as to whether the OH groups are picked up by the free valencies of carbon atoms from the moisture or are simply produced by the rearrangements of the atoms was still a matter of dispute which required a satisfactory explanation.

1.—An advocate of the peroxy acid theory might claim that the sodium salts of the unsaturated acids, containing more than one double bond in their structure, in the presence of air and under the catalytic action of moisture might form the hydroxyl groups; thus

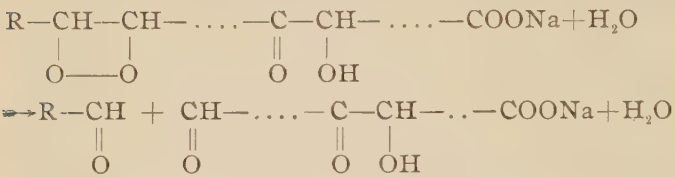


2.—A believer of the aldehyde theory might suggest the possibility of chemical reactions some what of the following type:

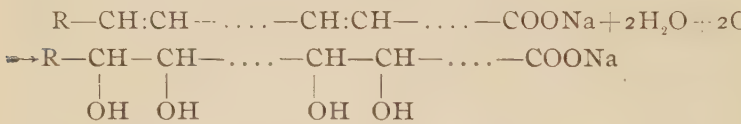
(a) Formation of OH group in the presence of air and under the catalytic action of moisture.



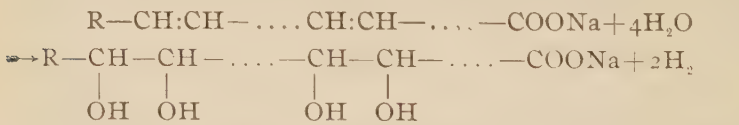
(b) Formation of aldehydes during the process of tanning:



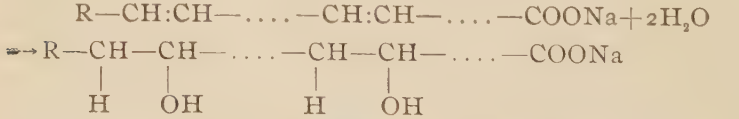
3.—The possibility of OH group might be attributed by some to the joint action of moisture and air; thus



4.—The presence of OH groups in the composition of the brownish soap might be said to be due to the action of moisture without the absorption of oxygen from the atmospheric air; thus



5.—Another possible condition giving rise to the formation of OH groups may be of the following nature.

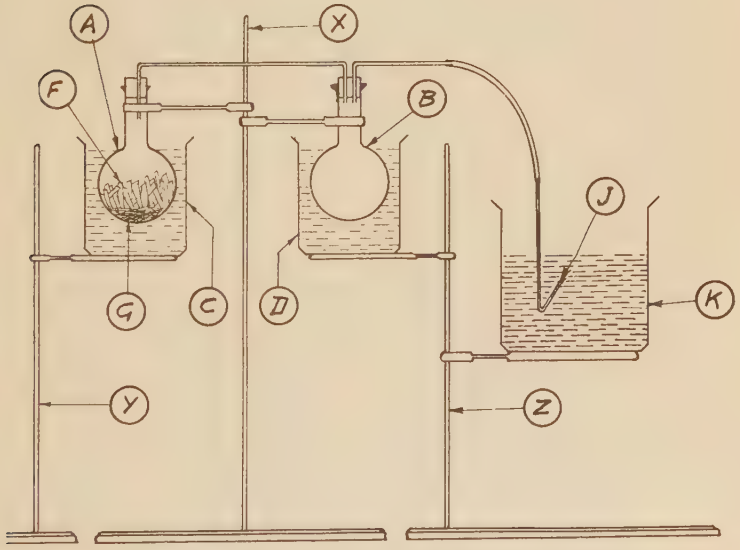


An examination of these theoretical reactions will show that if soap prepared freshly from seal oil be allowed to undergo chemical changes in an enclosed space containing air, then the pressure inside the space will be entirely dependent upon the nature of the

change. The reactions mentioned under cases 1, 2, and 3 will decrease the pressure, the reactions mentioned under case 4 will increase the pressure, while the reactions mentioned under case 5 will keep the pressure unaltered.

In order to get information from the changes in pressure an attempt was made to conduct some experiments in an enclosed space. A few grams of the soap (sodium salt) freshly prepared from seal oil was dissolved in a small quantity of distilled water and the pasty solution thus formed was thoroughly rubbed on the surface of pickled fleshers. These fleshers were then inserted in flask A, at the bottom of which the glass wool G had already been placed. Flask A and B, having a capacity of about 500 cc. each, were then attached to iron stands X, Y, and Z, and the whole apparatus made air tight as shown in the diagram (see Fig. 1).

Fig. 1.

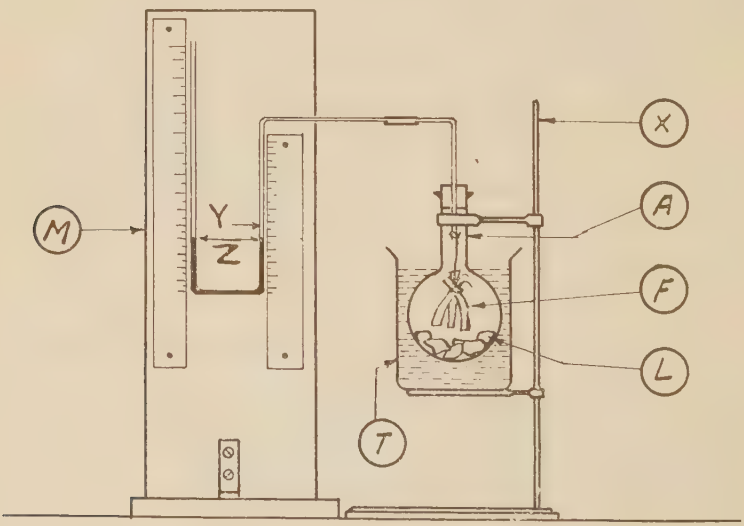


The temperature of the room as well as that of the apparatus was found to be 25° C. and at this temperature the jet J was closed. The tanning was thus allowed to take place in an enclosed space containing air. It had already been observed that the absence as

well as the presence of moisture in excess (approximately 30 per cent) are both detrimental for chamoising the hide substance and, consequently, in order to remove moisture from the fleshers F to the flask B and vice versa the temperatures of the flasks A and B were alternately changed by placing the containers C and D just under the flasks and by pouring warm (120° F.) and ice cold water into the containers at intervals. After five days the surface fibres of the fleshers had acquired a brownish tint. The temperature of the room being 25° C., the jet J was broken under the surface of colored water but no change in pressure was noticeable. Neither the colored water in the beaker K rose inside the tube above its surface, nor did any gas bubble through the liquid. After washing with a lukewarm solution (0.5 per cent) of sodium carbonate the surface of the fleshers was found to be in a partially tanned condition. During the process of tanning, therefore, gases are neither absorbed nor evolved.

To further verify the observations another test was made in which a liter flask A, containing about 350 grams of calcium chloride, was attached to a manometer M as shown in the diagram (see Fig. 2). A rectangular piece of cotton cloth (14" x 3.5")

FIG. 2.



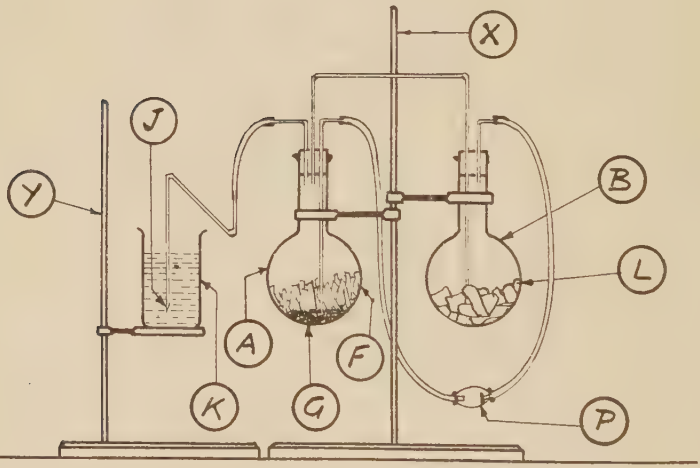
was moistened with water and a fairly large amount of the moist soap freshly prepared from seal oil was thoroughly rubbed on its surface. The moist piece was folded and hung inside the flask A, while the temperature of the room as well as that of the apparatus was 21° C. The pressure of the gases within the enclosed space was exactly equal to the atmospheric pressure, and consequently at room temperature the mercurial column in both the vertical tubes of the manometer was found to stand at Z. The temperature of the flask was then lowered to 6° C. by pouring a quantity of ice cold water in the container T. At this temperature the mercury was observed to stand at Y. The ice cold water was then withdrawn and the air tight apparatus was set aside for further observations. For the sake of comparison and contrast a blank test was also run under exactly similar conditions. After two weeks the soap under the influence of chemical actions had turned brown, but no appreciable amount of change in the pressure was noticeable. When the temperature of the flask A was again reduced to 6° C. the mercury was found to rise only .032 Cm. above the Y, as it also did in the blank test. The water vapours absorbed by the calcium chloride had created the slight change. Had oxygen or nitrogen been absorbed during the chemical reactions then the mercury would have been drawn into the flask. It is therefore evident that the gases of the atmosphere do not play any part in bringing about the chemical changes but that the particles of water are wholly and solely responsible for the formation of hydroxy compounds. Under these circumstances, therefore, the nature of the chemical reactions can be nothing but of the type mentioned under case 5 of theoretical reactions.

For the sake of further information, a few pieces of pickled sheep fleshers were moistened with water, and a fairly large amount of soap freshly prepared from seal oil, was thoroughly rubbed on their surfaces. The fleshers marked F (see Fig. 2) were then hung inside the flask A as a substitute for the cotton cloth and the same experiment along with the blank test was repeated a second time. After two weeks an appreciable amount of tannage was observed on the surface of the fleshers, while no change in pressure of any importance was noticeable. The rise of .02 cm. in the mercurial column of the manometer M was exactly equal to that of the blank test and it seems therefore evident

that the chemical reactions during the process of tanning hide substance are not accompanied by the evolution or absorption of any kind of gas.

From observations made in the previous experiments it seemed that when soap in contact with hide fibre is dehydrated, important change takes place. To determine the effect of such a change a few pieces of pickled sheep fleshers were moistened with water and a fairly large amount of moist (sodium salt) soap freshly prepared from seal oil, was rubbed on their surfaces. The flask A containing these fleshers F and the glass wool G (see Fig. 3)

FIG. 3.



was attached to the iron stand X and a few bags of cheese cloth containing about 200 grams of calcium chloride were inserted in flask B. The flask B containing the bags L was then connected with the flask A by means of glass and rubber tubing as shown in diagram. The whole apparatus with the exception of jet J was immersed in water the temperature of which was kept constant at 23° C. After an hour the jet J was closed and the whole apparatus containing a limited amount of air within an enclosed space was taken out of the water and set aside for the development of

chemical reactions. In the beginning the fleshers were too wet and no tannage was visible. The air inside the flask B was dead and moist and, in order to increase the rate of evaporation, air dried by means of calcium chloride was frequently circulated through the fleshers F by the pumping action of the rubber atomizer bulb P. By so doing the moisture from flask B was gradually transferred to that of A, until a point was reached when the moisture in the soap was found to be just sufficient for tanning purposes. At this stage the fleshers began to acquire slowly the characteristic yellow color of chamois leather and within a period of two days an appreciable amount of tannage was noticeable on their surfaces. The whole apparatus was again immersed in water and its temperature was reduced to 23° C. At this temperature the jet J was broken under the surface of colored water, but no change in pressure was noticeable. The surface of the colored water in the beaker K remained undisturbed. The fleshers F were taken out of the flask A, and, after being washed with a dilute solution (0.5 per cent) of sodium carbonate were found to be in a partially tanned condition. It can therefore, be safely concluded:

(a) That the real tanning material, *i. e.*, the hydroxy compounds are formed when the soap obtained from seal oil contains a limited amount (approximately 30 per cent) of moisture.

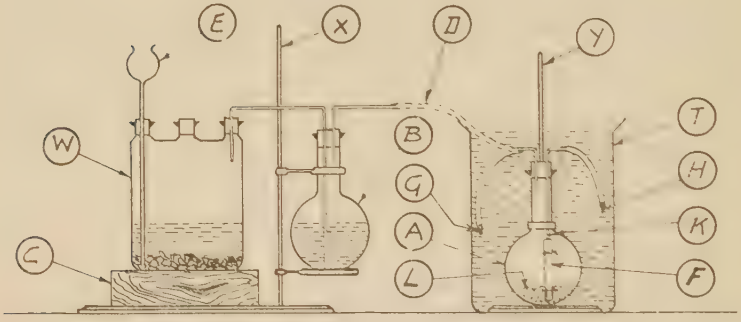
(b) Air plays no part in their formation and the reactions go to completion even, at the ordinary temperatures.

(c) These compounds combine with hide substance without the evolution or absorption of any kind of gas and the result of their mutual combination completes the manufacture of chamois leather.

In order to throw more light on the theory developed thus far, a few experiments were conducted in an enclosed space free from air. A rectangular piece of pickled sheep flesher was moistened with water and a fairly large amount of moist soap (sodium salt) freshly prepared from seal oil was rubbed on its surface. The rectangular piece F was tied to the verticle tube K and inserted in the flask A, after placing at its bottom L about 300 grams of calcium chloride. The trough T was filled with water and the flask A attached to the iron stand Y was placed at its bottom as shown in the diagram (see Fig. 4). In order to pass a stream of

hydrogen gas through the flask A, the rubber tubing D was connected with the delivery tube of flask B and the gas allowed to pass into flask A for about an hour. The ends G and H of the rubber tubing were then closed and the air tight flask, while still under the surface of the water, was set aside for further observations. The temperature of the water in the trough T was

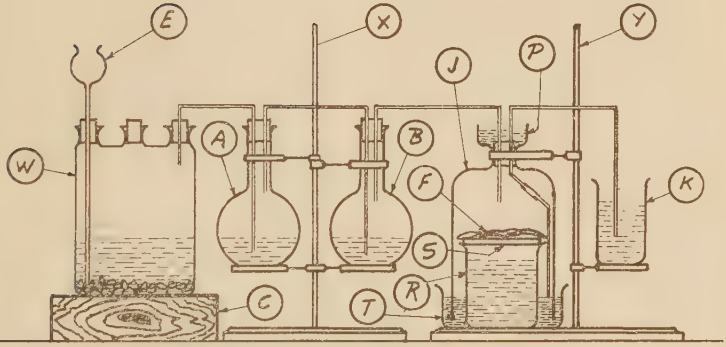
FIG. 4.



kept in the neighborhood of 30° C. After seven days flask A was taken out of the trough. The flesher F was found to have changed in its outward appearance and undergone a certain amount of tannage in spots. It was also noticed that the uncombined particles of the soap still adhering loosely to its surface had turned brown. The flesher was washed with a dilute solution of (0.5 per cent) sodium carbonate and dried in the air. At the end of these operations the surface fibres of the flesher at different places were found to have undergone an appreciable amount of tannage. The same experiment was repeated by using nitrogen and carbon-dioxide and the soap prepared from cod liver oil and shark liver oil in place of that prepared from seal oil, but in all the nine cases the signs of partial tannage were evident at different places on the surfaces of the fleshers. In order to get better and still more convincing results a circular piece of pickled sheep flesher was moistened with water and a fairly large amount of moist soap (sodium salt) freshly prepared from seal oil was

thoroughly embedded in its fibrous structure. The circular flesher F was then spread on the top of the desiccator plate S having a perforated surface. The circular trough T was filled with mercury and the beaker R containing concentrated sulphuric acid was placed in its centre. The top of the beaker was covered with the desiccator plate S and the bell jar J fitted with a cork and two glass tubes, was inverted into the trough as shown in the diagram (see Fig. 5). The Woulff bottle W and the flask A and B con-

FIG. 5.



taining concentrated sulphuric acid were connected with the bell jar J and in order to detect the leakage a small amount of colored water was poured into the cup P. The whole apparatus was made air tight and a current of hydrogen was circulated through it at a fairly constant speed. The gas after bubling through the concentrated sulphuric acid and passing through the bell jar was allowed to escape into the air. In about five hours the flesher had turned brown. The dry flesher was then taken from the bell jar and given another application of the moist soap and the same process repeated three times. The flesher as usual was treated with a lukewarm (110° F.) solution of (0.5 per cent) sodium carbonate, then washed with plain water and finally dried in the air. After undergoing all these operations the fibres of the flesher,

were found to be in a tanned condition. They were soft and pliable, brownish in color, resistant to water and in fact had all the characteristic properties of a chamois leather. In order to throw more light on the subject, a few more experiments the results of which are given in tabular form were also performed and a review of all the tests and observations made so far clearly show that:

TABLE SHOWING THE RESULTS OF DIFFERENT EXPERIMENTS PERFORMED TO CHAMOIS PICKLED AND MOIST SHEEP FLESHERS IN A CURRENT OF HYDROGEN GAS.

No.	Materials used for tanning the fleshers	Approximate temperature at which the experiment was conducted	Observations
1	Soap (sodium salt) prepared freshly from cod liver oil	80° F.	Satisfactory Tannage
2	Soap (sodium salt) prepared freshly from shark liver oil	80° F.	Satisfactory Tannage
3	Soap (sodium salt) prepared freshly from linseed oil	80° F.	Tannage (fairly good)
4	Fatty acids obtained from seal oil	110° F.	Tannage Indicated
5	Fatty acids obtained from cod liver oil	110° F.	Tannage Indicated
6	Seal oil	120° F.	Satisfactory Tannage
7	Cod liver oil	120° F.	Satisfactory Tannage

N. B. In each case three applications of the tanning materials were given to the fleshers and the fleshers in the end were first treated with luke-warm (110 F.) solution of (0.5 per cent) sodium carbonate then washed with water and finally dried in air. In order to get better results the fleshers should be thoroughly dried in the current of hydrogen Rapid drying should be avoided; but if it does take place then a mere application of a slight amount of water, without tanning materials to the fleshers will prove useful.

(a) the gaseous ingredients of the air do not play any part in chamoising a moist skin other than that of removing the mechanically held water from within the fiberous structure of the hide substance.

(b) If we adopt the reduced formula $R'NH_2$ for the hide substance, and assume for a while ordinary oleic acid $CH_3.(CH_2)_7.CH:CH.(CH_2)_7.COOH$ to be the chief ingredient of seal oil, then the chemical reactions which will come into play during the process of tanning will be of the following nature:

In case of unsaturated oil:

1. $CH_3.(CH_2)_7.CH{:}CH.(CH_2)_7.CO.OCH_2$
$CH_3.(CH_2)_7.CH{:}CH.(CH_2)_7.CO.OCH$ $+ 3H_2O$ X
$CH_3.(CH_2)_7.CH{:}CH.(CH_2)_7.CO.OCH_2$
Triolein

$\rightarrow 3\{CH_3.(CH_2)_7.CH{:}CH(CH_2)_7.COOH\} + CH_2OH.CHOH.CH_2OH$
Oleic acid Glycerine

2. $CH_3.(CH_2)_7.CH{:}CH.(CH_2)_7.COOH + H_2O$
Oleic acid
$\rightarrow CH_3.(CH_2)_7.CH(H).CH(OH).(CH_2)_7.COOH$ ..... Y
Hydroxystearic acid

3. $CH_3.(CH_2)_7.CH(H).CH(OH).(CH_2)_7.COOH + R'NH_2$
Hide substance
$\rightarrow CH_3.(CH_2)_7.CH(H).CH(R'NH).(CH_2)_7.COOH + H_2O$ ..... Z

In case of unsaturated acid:

The chemical reactions in this case are similar to Y and Z.

In case of the sodium salt of the unsaturated acid:

1. $CH_3.(CH_2)_7.CH{:}CH.(CH_2)_7.COONa + H_2O$
Sodium salt of oleic acid
$\rightarrow CH_3.(CH_2)_7.CH(H).CH(OH).(CH_2)_7.COONa$
Sodium salt of hydroxystearic acid

2. $CH_3.(CH_2)_7.CH(H).CH(OH).(CH_2)_7.COONa + R'NH_2$
Hide substance
Sodium salt of hydroxystearic acid
$\rightarrow CH_3.(CH_2)_7.CH(H).CH(R'NH).(CH_2)_7.COONa + H_2O$
Water

(c) Hydroxy acids, the formation of which is essential to the chamoising of hide substance, are not formed in excess of water.

(d) Hydrolysis of unsaturated oils accompanied by the removal of glycerine, does not take place easily at a low temperature. It is a matter of common experience that unsaturated oils during the process of tanning, generate heat and evolve a very large amount of volatile and pungent product, especially acrolein formed by the dehydration of glycerine,[18] which irritates the eyes to a great extent. Garelli and Apostolo[19] confirmed in 1913 that the neutral glycerides (*i. e.*, oils) have only a mechanical action and cannot chamois hide substance. The oils hydrolyse on the surface of the animal fibres, and Andre Piedallu[20] attributes this change to the action of micro-organisms. He found the Fungus Monascus Olei on hides undergoing chamoising and ascribes the hydrolysing action of the oils to an oxydase secreted by the fungus. The unsaturated acids thus liberated on the surface of the moist skin, according to recent theories are supposed to absorb oxygen from the air; but this assumption has now been found to be erroneous.

The results of the present investigation conclusively prove (1) that the unsaturated acids combine chemically with the molecules of water present in the moist skin; (2) the products of combination form the hydroxy-acids of the type shown, and (3) in the end the mutual combination of the hide substance with the hydroxy-acids results in the elimination of water which completes the production of chamois leather.

An attempt was next made to ascertain the tanning power of the sodium salt of $CH_3.(CH_2)_7.CH.(OH).CH.(OH).(CH_2)_7.COOH$ prepared from the dihydroxystearic acid. Oleic acid of the formula $CH_3(CH_2)_7.CH:CH.(CH_2)_7.COOH$ seems to be incapable of chamoising hide substance. It has only one double bond in its structure, and, consequently does not absorb oxygen from the air. Under such circumstances, the theories which base the efficiency of oil-tannage on the formation of aldehydes or peroxyacids, would naturally necessitate the presence of at least two double bonds in the composition of the tanning materials. Although it has now been proven that the presence of oxygen is not needed for chamoising hide substance, the problem regarding the

[18] Proctor. "Principles of Leather Manufacture," p. 458. D. Van Nostrand Co., New York, (1922).

[19] F. Garelli and C. Apostolo. *Collegium*, pp. 425-428 (1913).

[20] A. Piedallu. *Compt. rend.*, 151, 397 9 (1910).

number of double bonds necessary for the effective tannage was one which still required adequate solution.

For the sake of conducting the experiment, a sample of olive oil of unquestionable purity was obtained. The liquid glycerides of this pure product were formerly thought to consist of trioleine alone, but the presence of linoleic acid[21] (as much as 7 per cent, this explaining the high iodine number of the oil) has now been proven. It was, therefore, necessary to devise some means to isolate the dihydroxy-stearic acid in a state of purity, and, in order to do so, about 32 grams of the olive oil was changed into the solid hydroxy acids by following the same procedure previously described. The solid acids thus obtained were extracted with ether and the ethereal extract containing the unoxidized portion of the oil, together with lower fatty acids and azalic acid, was entirely discarded. The insoluble portion containing the dihydroxy-stearic acid in a contaminated form was then extracted with hot water (90° C.) and the traces of tetra-hydroxy-stearic acid thus removed. The portion insoluble in hot water, being pure dihydroxy-stearic acid was then treated on a water bath with 30 cc. of an aqueous solution of sodium hydroxide, having a specific gravity of 1.28. Glass beads were used to avoid bumping and during the process of saponification about 1500 cc. of boiling water were gradually added with constant stirring. The soapy solution, while still hot, was passed through a filter paper. The residue left on the filter paper was discarded while the filtrate containing the sodium salt (*i. e.*, soap) of the dihydroxy-stearic acid in solution was evaporated to about 400 cc. The concentrated solution on cooling was salted out, and the salt of the acid which is sparingly soluble in water, was thus separated. It was then agitated with distilled water, and the soapy emulsion thus formed was used for experimental purposes. A small rectangular piece of pickled sheep flesher was moistened with water and the soapy emulsion thoroughly rubbed on its surface. The piece was then dried at room temperature and given about twenty applications of the dilute emulsion. The dried flesher was then treated with a lukewarm (110° F.) solution of (0.5 per cent) sodium carbonate and finally washed with distilled water. It was again dried in air and the air-dried flesher subjected to the solvent actions of

[21] K. Hazura and A. Grussner. *Monatsh. Chem.*, 9, pp. 944-946.

ether and chloroform. At the end of these operations the fibres of the flesher, which in this case had acquired a somewhat whitish appearance, were found to have undergone an appreciable amount of tannage. They were opaque, soft, and flexible, and the surface of the flesher had entirely lost that jelly-like structure which is the inherent property of an untanned skin. The experimental results, therefore, show:

(a) That no restriction regarding the number of unsaturated bonds can deprive an acid of its tanning properties;

(b) Even the sodium salt of ordinary oleic acid having the hydroxy groups (OH) attached to its carbon atoms number 9 and 10, is capable of tanning animal fibre;

(c) The materials suitable for tanning purposes, while in the form of unsaturated acids, must be sensitive enough to pick up the hydroxy group from the moisture;

(d) The number and the reactive positions of the hydroxyls attached to the free valencies of the fatty acids, seem to play definite roles in the chamoising of hide substance.

For the determination of the tanning power of a mixture of α and β hydroxy-stearic acids about 200 cc. of oleic acid dissolved in 400 cc. of redistilled gasoline of approximately 60° Be was treated slowly with 32 cc. of concentrated sulphuric acid at a temperature not exceeding 4° C. The products of chemical actions are indicated by the following equations:

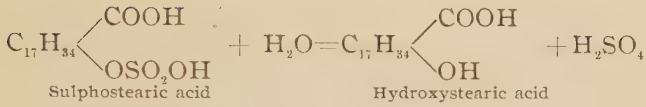
(a) $C_{17}H_{33}COOH + H_2SO_4 = C_{17}H_{34}(COOH)(OSO_2OH)$

Oleic acid — Sulphostearic acid

(b) $C_{17}H_{33}COOH + H_2SO_4 = C_{17}H_{34}(CO{-}O) + H_2SO_4$

Oleic acid — Stearolactone

These products were then subjected to the action of live steam, whereby the unchanged petroleum distillate was evaporated while the sulphostearic acid was decomposed in accordance with the following equation:



The resulting mixture was allowed to cool, and, after standing for a short time, the layer of the aqueous sulphuric acid was drawn off. The remaining mass, containing the hydroxystearic acid, stearolactone, and unaffected oleic acid, was extracted with hot petroleum naphtha. On cooling the extract to about 4° C., the hydroxystearic acid crystallized as a white mass, leaving behind the other compounds in solution. The white crystals of

α—$CH_3.(CH_2)_{15}.CH.(OH).COOH$ and

β—$CH_3.(CH_2)_{14}.CH.(OH).CH_2COOH$

hydroxystearic acids thus separated, were thoroughly washed with cold petroleum naphtha, and, after drying, were used for experimental purposes.

A small rectangular piece of pickled sheep flesher was moistened with water and the alcoholic solution of the solid acids was thoroughly rubbed on its outer surface. The flesher was dried in the air at room temperature (30° C.) and given about twelve applications of the alcoholic solution. The flesher was then treated with a lukewarm (110° F.) solution (0.5 per cent) of sodium carbonate and ultimately washed with distilled water. It was again dried in air, but did not show any sign of tannage. An attempt to tan a pickled sheep flesher with the sodium salts of the α and β hydroxy-stearic acid also met with failure.

From the tanning point of view, therefore, the hydroxyl (OH) groups attached to the α or β carbon atoms seem to be in the most inactive positions.

Finally as to the number and positions of hydroxyl (OH) groups in the composition of higher fatty acids and their effects on tanning hide substance, it should be noted that the unsaturated acids of seal oil, according to Ljubarsky[22] yield on oxidation a mixture of dihydroxy-palmitic and dihydroxy-stearic acids, from which he inferred the presence of oleic acid and physetolic (or hypogaeic) acid in the original oils. Both of these acids have only a single double linkage in their structure, and, consequently, if the analysis of Ljubarsky be considered as authentic, then it can

[22] Ljubarsky. *Journ. F. Prakt.* Chem. 26 (1898).

be safely concluded that even the presence of one double union in an unsaturated acid is sufficient for chamoising hide substance. However, because the fatty acids obtained from seal oil seem to absorb a somewhat higher percentage of iodine than the expected amount, Bull and some others are of the opinion that seal oil must contain a comparatively small amount of highly unsaturated acids also. As a matter of fact, the degree of unsaturation in a higher fatty acid ought not to be judged by its iodine value alone. Oleic acid, for example, can exhist theoretically in sixteen different forms;[23] fifteen of which may also exist in their stereoisomeric form of elaidin acids, making a total 31. The iodine values of these isomeric acids seem to increase as the position of the double linkage moves further from the carboxyl group (COOH). It was found in 1913 that the iodine value[24] of 2.3 oleic acid is 9.04: of 3.4 oleic acid is 16.27: and of 4.5 oleic acid is 26.96: while the normal value of 9.10 oleic acid is 89.4 Lewkowitsch[25] finds by comparative tests, that the proportion of iodine absorbing capacity to oxygen absorbing capacity, is two atoms of iodine to one atom of oxygen multiplied by 0.0632. Applying this formula to fish oils, the iodine number, says Schlosstein,[26] has very often proved to be misleading in establishing their drying qualities. As a matter of fact, fish and liver oils[27] absorb approximately as much iodine as do the best drying oils, yet they are greatly inferior to the latter as regards the power of oxygen absorption. Furthermore, fish and liver oils differ materially from the "drying oils" in that they do not form a skin as does linseed oil. For ascertaining whether a "cod oil" is suitable or otherwise for use in the tanning industry Liotman and Peters[28] conducted a series of experiments and showed that as the oxidation value increases the more unsuitable becomes the oil for leather making. Good oils gave oxidation figures of 10 to 25; while those which are useless give figures ranging from 46 to 85. It should be further noticed that hydrocarbons have no tanning value, but their presence in

[23] W. Fahrion. *Chem. Umschau,* 23, 2-8 (1916).

[24] A. Eckert and O. Halla. *Monatsh. Chem.,* 34, 1815-1824 (1913).

[25] Lewkowitsch. "Chemical Technology and Analysis of Oils, Fats and Waxes." Sixth Edition, Vol. 1, p. 478. Macmillan & Co., Limited, London. (1921).

[26] H. Schlosstein. Shoe and Leather Rep. (1918) reprinted in *J. A. Leather Chem. Ass.,* 14, 41-49 (1919).

[27] Lewkowitsch. "Chemical Technology and Analysis of Oils, Fats and Waxes." Sixth Edition, Vol. 1, p. 485. Macmillan and Co., Limited, London. (1921).

[28] Liotman and Peters. *J. Soc. Chem. Ind.,* 693 (1902).

fish oils changes their iodine numbers. Shark oil for example contains sequalene,[29] which being a highly unsaturated hydrocarbon raises its percentage of iodine absorption. A new hydrocarbon named by Chapman as "Spinacene"[30] has also been obtained from certain fish liver oils. All these discrepencies, therefore, show that the iodine value of a fish oil, in no way, can be looked upon as a criterion for determining its suitability for tanning leather.

Consider now the following points:

(a) Seal oil on mild oxidation yields hydroxy-acids of such a nature that they can be obtained only from unsaturated fatty acids having but one double union in their structure.

(b) The sodium salt of ordinary oleic acid having the hydroxyl groups (OH) attached to its carbon atoms number 9 and 10, is capable of chamoising hide substance.

(c) The hydroxy acids formed from the unsaturated acids of the oleic series, in an alkaline solution of potassium permanganate, and having the number of hydroxyl groups (OH) equal to the number of free valencies originally present in the unsaturated acids, do not show as much power of tanning as those formed from the same unsaturated acids under the influence of moisture, and thus having only one half the number of such hydroxyl groups (OH) in their composition.

(d) The iodine value of unsaturated isomeric acids increases as the position of the double linkages moves further from the carboxyl group.

(e) The α and β hydroxy-stearic acids having the position of their hydroxyl groups (OH) in the most inactive place, play no part in the chamoising of hide substance.

From these facts it can be safely concluded that the best tanning agents among the fatty acids belonging to the oleic series are those which occupy the position of their single double union in a reactive place. The mono-hydroxy acids combining with one molecule of hide substance ($R'.N.H_2$), tan better than di and tetra hydroxy acids combining with two and four molecules of hide substance respectively. The positions of the bonds between carboxyl and the ninth carbon atom are not very active, while the

[29] Mitsumaru Tsujimoto. *J. Ind. Eng. Chem.*, Vol. 12, No. 1; p. 63, (1920).
[30] A. C. Chapman. *J. Chem. Soc. Trans.*, p. 56, (1917); p. 458, (1918).

bonds existing between the carbon atoms away from the ninth, combine with water even at ordinary temperatures. The farther a bond is from the ninth carbon atom, the better it seems to work in the formation of hydroxy acids—a property which makes the fish oils so useful for tanning purposes.

A brief review of the inner working of the tanning materials will show that the unsaturated oils capable of chamoising hide substance first hydrolyse on the hide fiber, and the rise in temperature facilitates the hydrolysis to a greater extent. Since, at a temperature over 130° F., hide fibers in the presence of moisture, are destroyed, the moist skins, after being rubbed with oils, are generally dried in the neighborhood of about 120° F. The unsaturated acids thus set free, having at least a single double linkage in a reactive position, chemically combine with the hydroxyl of the moisture; and the saturated acids, chiefly monohydroxy acids, thus formed, combine at 120° F. with the hide substance with the elimination of water at a fairly rapid rate. Skins dried at ordinary temperatures show signs of tannage after a prolonged time; while the lack of moisture under the influence of chemical affinity, causes the dehydration of the fibres themselves, which finally results in a weakening of the finished product. The uncombined oil held within the interstices of the skin, lubricates the partially or wholly tanned fibres and increases their strength, but when changed into acid after a prolonged time, it loses this advantageous property and renders the fibres hard and weak.

The metallic salts have also been shown to have a tanning value, and the experimental data further demonstrate conclusively that neither the oxygen nor the nitrogen of the air plays any chemical part in the formation of oil-tanned leather. The oils inside the blubbers detached from the freshly killed seals (callorhinus Alascanus) hydrolyse and goes on changing in the presence of moisture into hydroxy acids with the passage of time. These hydroxy acids impart a brownish tint to the oil and it is, therefore, that the dark oils possess comparatively a superior power of tanning over the pale oils rendered at the Island from the blubbers of the freshly killed seals. Cod liver oils and shark liver oils also change their appearance in the presence of moisture.

The unsaturated acids obtained from linseed oil are also capable of chamoising hide substance and it therefore, seems evident

that the origin of oils has nothing to do with their tanning properties.

Summary

The hydroxy acid theory of oil tannage:—Up to the present time the prevailing theories of oil-tannage base the tanning reactions upon the absorption of oxygen by the tanning materials, but the experiments herein specified, quite conclusively prove that the mechanism of oil tanning is not in accord with this conjecture.

This investigation demonstrates that the basic principle of the theory of oil tannage is the formation of hydroxy-compounds within the fibrous structure of the hide substance. The oils, when used for tanning purposes, hydrolize on animal fibre. The fatty acids thus set free, belong chiefly to the oleic series or at least one double union in their structure occupies a very reactive position. The two free valencies of carbon atoms comprising the union combine chemically with H and OH radicals of the water molecules which are always present in the moist skin during the process of tanning. The mono-hydroxy acids thus formed, combine chemically with hide substance with the elimination of water, which completes the principle chemical reaction in the manufacture of chamois leather. The hydroxy acids containing two or more than two hydroxyls in their structure and consequently combining with two or more than two molecules of hide substance produce leather of an inferior quality and poorer feel. In oils used for tanning purposes therefore, the acids containing a single double bond are the ones which are the most essential in chamoising the hide substance.

Vita

Bishan Narain Mathur was born in October, 1883, in Lahore, the Capital of the Province of Punjab, India. After attending the High Schools and Colleges of that City he, at the age of 26, adopted the line of teaching as his profession. After fulfilling all the requirements, he was awarded in 1914 the Diploma of S. A. V. by the Central Training College, Lahore, and shortly afterwards was appointed by the University of the Punjab, as an Examiner in Practical Science. He held this position for a period of six years, until 1921 when he left India for the further prosecution of his studies.

Realising, after his 11 years' of experience as a teacher, the value of technical training, he joined the Pratt Institute, Brooklyn, New York, and on completion of its full two years' Course, was awarded in June 1923 the Diploma of Industrial Chemical Engineering. Since then up to the present time he has been studying under the Faculty of Pure Science of Columbia University, from which he received the degree of M. A. in 1924.

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